

PATENT SPECIFICATION

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(54) IMPROVEMENTS IN SHOE MANUFACTURE

(71) We, THE SHOE AND ALLIED
 TRADES RESEARCH ASSOCIATION,
 a British company, of Satra House,
 Rockingham Road, Kettering, Northants,
 do hereby declare the invention, for
 which we pray that a patent may be
 granted to us, and the method by which
 it is to be performed, to be particularly
 described in and by the following state-
 ment:—

The present invention relates to the
 adhesion of elastomeric materials, and in
 particular to the attachment of shoe sole
 material to shoe upper material such as
 leather.

It is known that the receptiveness of
 elastomeric soling material (e.g. natural
 rubber, styrene-butadiene rubber, nitrile
 rubber, and mixtures and blends of these),
 towards adhesives of, e.g. polychloroprene
 and polyurethane types, is often unsatis-
 factory. Modern methods of shoemaking
 frequently employ stuck-on soles, as
 opposed to the traditional stitched-on
 leather sole and hence the problem of
 ensuring good adhesion of the sole to the
 upper is of considerable importance.

British Patent Specification Nos.
 1,278,258, 1,295,677, and 1,295,842 describe
 various ways of improving adhesion by halo-
 genating the rubber surface e.g. through the
 use of an organic halogen donor which
 liberates halogen slowly.

The treatment described generally
 consists of wiping or dipping the elastomeric
 sole material in a solution containing the
 halogen donor, after which the sole is dried
 and can be stored prior to attachment to the
 shoe upper. A sole may be precemented
 after such treatment and subsequently heat
 activated before securement.

It has been proposed in British Patent
 Application No. 54751/72 (Serial No.
 1458007) to incorporate in a polyurethane
 adhesive both a small proportion of an
 organic bromine donor and an organic
 isocyanate or "primer". The adhesive so
 formulated gives rise to acceptable creep

resistance at elevated temperatures. The
 invention of the latter application is of
 particular value for bonding thermoplastic
 rubbers of the block-copolymer type as no
 pretreatment of the bonding surface is
 necessary before application of the
 adhesive.

The inventions of the above-mentioned
 patent specifications are entirely concerned
 with the adhesion, e.g. to shoe uppers of
 ready-made moulded soles.

An alternative practice has now arisen of
 directly injection moulding thermoplastic
 elastomer soles to shoe uppers in a similar
 manner to the relatively older practice of
 the injection moulding *in situ* of PVC soles.
 By "thermoplastic elastomer" is meant
 generally any injection mouldable rubber-
 like material.

The present invention, as will become
 apparent, is concerned with thermoplastic
 elastomers containing EVA (ethylene-vinyl
 acetate copolymer) whether in pure form or
 admixed with other thermoplastic elasto-
 mers and/or compounding materials.

There are two principle types of EVA
 soling compounds used as shoe solings. The
 first is a crosslinked EVA usually micro-
 cellular in character, where the cross-
 linking is usually effected by peroxides.
 Such compounds can be bonded relatively
 easily by mechanically scouring the surface
 and then using a polychloroprene adhesive,
 or by wiping the mechanically prepared
 surface with an isocyanate primer prior to
 using a urethane adhesive. Alternatively it is
 possible to use a two-part urethane adhesive
 (a urethane adhesive to which an isocyanate
 has been added) on a mechanically
 prepared surface.

Good adhesion to thermoplastic EVA
 soling compounds is very much more
 difficult to achieve. We have found that a
 simple isocyanate treatment, a halogenat-
 ing treatment, or a mixed isocyanate plus
 halogenation treatment is ineffective in
 promoting good adhesion. We have
 however unexpectedly found that good

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bonds to injection moulded thermoplastic EVA compounds can be obtained by treating the surface with a composition which can be used as a primer or directly as an adhesive.

According to one form of the invention there is provided a method of shoe making in which an EVA-containing sole is injection moulded in situ onto a shoe upper, wherein the upper is treated with a composition comprising a mixture of a chlorinated polyolefin and a thermoplastic EVA, together with an adhesive if necessary. Preferably the mixture includes an organic polyisocyanate (as defined herein).

In particular, good bonds can be obtained by treating the upper surface with a solution of a mixture of a chlorinated polyolefin (such as that sold under the Eastman-Kodak product name CP 343-1 or chlorinated rubber as that sold by ICI under Trademark Alloprene N20), and thermoplastic ethylene vinyl acetate copolymer (hereinafter called EVA copolymer) (such as that sold under the ICI product name EVA Resin 28-20) in xylene or other solvent followed by treatment of the surface with an organic polyisocyanate (such as 4-4' diphenylmethane diisocyanate e.g. as sold under the Trademark Caradate 30). By "poly" we mean two or more. The adhesion to such a prepared surface with a single or two-part urethane adhesive at used in the shoemaking industry (such as that sold under the trade name B.U. 8300) will be good. The concentration of chlorinated polyolefin and EVA copolymer in the solution can vary independently e.g. from 0.1% to 30% w/v, and the concentration of Caradate 30, for example in MEK, can vary e.g. from 1% to 30% w/v.

In order to simplify the bonding procedure we have found that it is possible and preferable to combine the two surface primers for use as a single primer. This mixed primer may comprise e.g. from 0.1% to 30% w/v of a chlorinated polyolefin plus e.g. from 0.1% to 30% of EVA copolymer plus e.g. from 0.1% to 30% w/v of the polyisocyanate dissolved in xylene or other aromatic solvent or solvent blend. Normally the total solids content of a primer solution will be from 5 to 10% w/v. After application of this primer a good bond is obtainable with a urethane adhesive. Normally it is not contemplated that the total of the three ingredients will exceed 30% w/v. However situations are possible where the primer will act similarly to an adhesive and in such cases the total content of the three ingredients may rise to 20% w/v or more.

The composition of the invention may be used in a solvent free or melt form, e.g. as a pre-cast film of adhesive. In melt adhesives blocked isocyanates are preferred. The

solvent (when used) should be compatible with both primers and aromatic solvents can be used or e.g. chlorinated hydrocarbon solvents or solvent blends, e.g. of aromatic solvents and non-aromatic solvents of which a blend of three parts toluene to 1 part ethyl acetate is particularly suitable.

The vinyl acetate content of the EVA soling compound appears to influence the response to both methods of surface treatment and we consider that the vinyl acetate content should preferably be not less than 12 or more preferably 16% to ensure that these treatments are effective. The use of chlorinated rubber produces better response to low vinyl acetate copolymers than e.g. CP 343-1.

The mixed chlorinated polyolefin-EVA copolymerisocyanate primer, in particular, can be used to effect the bond between an upper material such as PVC, polyurethane or leather and an injection moulded-on EVA soling compound.

The upper material may be coated with a urethane adhesive such as that sold under the Trademark B.U. 8300. This adhesive coated upper material is left for the adhesive to dry e.g. for 1 hour although longer drying periods can be used. The adhesive surface is then wiped with a xylene solution containing chlorinated polyolefin EVA copolymer and isocyanate. The treated adhesive surface is then left for at least 5 minutes before injection on the EVA soling compound. The concentration of chlorinated polyolefin and EVA copolymer in the xylene can vary independently e.g. from 0.1% to 30% w/v and the concentration of isocyanate can vary e.g. from 1% to 30% w/v.

In the Examples shown in Table 1, EVA compound UE 634 (Chemitrade Ltd) was injection moulded onto a full chrome upper leather (Steads Pearl Split), a PVC coated fabric (Blakes 47 thou patent PVC on S.D.1.), and a poromeric upper material (Porvair Limited) using the following procedure:—

Example 1.

Leather — The surface to be treated was roughened with a wire brush and coated with urethane adhesive B.U. 8300 and left for 1 hour open time. A xylene solution containing 1.4% chlorinated polyolefin CP 343-1 plus 2.6% EVA Resin 28-20 plus 2.5% w/v Caradate 30 was applied to the adhesive surface. The treated leather was left for 5 minutes and 30 minutes respectively before injecting-on the UE 634 EVA soling compound.

Example 2.

P.V.C. — The surface was wiped with MEK and coated with urethane adhesive

- B.U. 8300 and left for 1 hour open time. A xylene solution containing 1.4% w/v chlorinated polyolefin CP 343-1 plus 2.6% w/v EVA Resin 28-20 plus 2.5% w/v 4-4' diphenylmethane diisocyanate (Caradate 30) was applied and left for 5 minutes and 30 minutes respectively before injecting on the UE 634 EVA soling compound.
- 5 The moulded constructions were left for 7 days before testing by the SATRA peel test. It is possible in injection moulding EVA to eliminate the use of the urethane adhesive and to use instead a stronger solution of the primer as the adhesive on the upper (see Table 3).
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- 10 Porvair (Trade Mark) — The surface was roughened with a wire brush and coated with urethane adhesive B.U. 8300 and left for 1 hour open time. A xylene solution containing 1.4% w/v chlorinated polyolefin CP 343-1 plus 2.6% w/v EVA Resin 28-20 plus 2.5% w/v 4-4' diphenylmethane diisocyanate (Caradate 30) was applied and left for 5 minutes and 30 minutes respectively before injecting on the UE 634 EVA soling compound.
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- 15 Upper materials leather, PVC and Porvair were prepared as described in Examples 1, 2 and 3 respectively. The prepared surfaces were then each coated with a xylene solution containing 7% w/v chlorinated polyolefin CP 343-1 plus 13% w/v EVA Resin 28-20 plus 5% w/v 4-4' diphenylmethane diisocyanate (Caradate 30) and left for 1 hour open time before injecting on the UE 634 EVA soling compound.
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TABLE 1

ADHESIVE	TIME BETWEEN PRIMING AND MOULDING	Example 1 LEATHER UPPER		Example 2 PVC UPPER		Example 3 PORVAIR UPPER	
		LOAD kgf/cm	TYPE OF FAILURE	LOAD kgf/cm	TYPE OF FAILURE	LOAD kgf/cm	TYPE OF FAILURE
B.U. 8300	No prime	0.8	10SSM 90ASM	0	100ASM	0.2	100ASM
	5 mins	6.2	5SSM 95ASM	6.2	15SSM 40ASM 45AUP	5.0	100ASM
	30 mins	7.4	10SSM 90ASM	7.5	100ASM	5.9	100 ASM

Key: — ASM — failure of adhesion to soling material

SSM — surface soling material failure

AUP — failure of adhesion to upper plastic

TABLE 2

ADHESIVE	OPEN TIME OF ADHESIVE OF UPPER	Example 4 LEATHER UPPER		Example 5 PVC UPPER		Example 6 PORVAIR UPPER	
		LOAD kgf/cm	TYPE OF FAILURE	LOAD kgf/cm	TYPE OF FAILURE	LOAD kgf/cm	TYPE OF FAILURE
7% chlorinated polyolefin CP 343-1 plus 13% EVA, (I.C.I. 28-20) plus 5% Caradate 30	1 hour	3.4	20SM 80AUC SM tore	9.7	25SM 75AUP	5.9	100AUM UM tore
	2 hours	8.4	80SM 20AUC SM tore	4.3	100 AUP	6.9	55M 95AUM UM tore

Key:— SM — soling material failure

AUC — adhesion to upper leather failure

AUP — adhesion to upper material failure

AUM — adhesion to upper material failure

SM tore — soling material failure tore

UM tore — upper material tore

WHAT WE CLAIM IS:—

1. A method of shoe making in which an EVA-containing sole is injection moulded in situ onto a shoe upper, wherein the upper is treated with a composition comprising a mixture of a chlorinated polyolefin and a thermoplastic EVA, together with an adhesive if necessary. 25
2. A method as claimed in claim 1 wherein the mixture includes an organic polyisocyanate (as defined herein). 30
3. A method as claimed in claim 1 or claim 2 wherein the composition is in the form of a solution of the said mixture in a solvent and is applied as a primer, wherein the total solids content of the solution does not exceed 30% w/v. 35
4. A method as claimed in claim 3 wherein the solution has a total solids content of 5% to 10% w/v.
5. A method as claimed in claim 2 wherein the composition is in the form of a solution of the said mixture in a solvent, and is applied as an adhesive, wherein the total solids content of the solution is 20% w/v or more. 25
6. A method as claimed in any of claims 3, 4 or 5 wherein the solvent used in the solution comprises xylene or a blend of an aromatic solvent with a non-aromatic solvent. 30
7. A method as claimed in any preceding claim wherein the chlorinated polyolefin is chlorinated natural rubber.
8. A method as claimed in any preceding claim substantially as described herein with reference to any one of the Examples. 35
9. A shoe prepared by a method as claimed in any preceding claim.

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